



ADDITION AND TO ATTOM PUBLISH	HED I	NDER THE PATENT COOPERATION TREATY (PC1)	
		WO 96/17104	
(51) International Patent Classification 6:		(11) International Publicati n Number: WO 90/1/104	
C23C 16/34, H01L 21/285, 21/28, 21/3205, 21/768, 29/47	A1	(43) International Publication Date: 6 June 1996 (06.06.96)	
(21) International Application Number: PCT/US		CH, CN, CZ, DE, DK, EE, ES, TI, OD, OZ, TI, MD	
(22) International Filing Date: 30 November 1995 (MG, MK, MN, MW, MX, NO, NZ, PL, P1, RO, RO, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, Europear		
(30) Priority Data: 08/348,646 30 November 1994 (30.11.5	94) 1	MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE LS, MW, SD, SZ, UG).	
(71) Applicant: MICRON TECHNOLOGY, INC. [US/US Federal Way, Boise, ID 83706-9632 (US).	s]; 800 0	Published	
(72) Inventors: MEIKLE, Scott; 1301 East Jefferson, 83712 (US). DOAN, Trung; 1574 Shenandoah Dri ID 83712 (US).	Boise, ive, Bo	With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt amendments.	
(74) Agent: FLETCHER, Michael, G.; P.O. Box 4433, Ho	ouston,	rx	

(54) Title: A METHOD OF DEPOSITING TUNGSTEN NITRIDE USING A SOURCE GAS COMPRISING SILICON

(57) Abstract

77210 (US).

A method for depositing tungsten nitride uses a source gas mixture having a silicon-based gas for depositing the tungsten nitride to overlie a deposition substrate. A non-planar storage capacitor has a tungsten nitride capacitor electrode.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

	Austria	GB	United Kingdom	MR	Mauritania
AT		GE	Georgia	MW	Malawi
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazit	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic	NJ	of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SI	Slovenia
CH	Switzerland		Marathuran	SK	Slovakia
CI	Côte d'Ivoire	KZ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	TD	Chad
CN	China	LU	Luxembourg	TG	Togo
CS	Czechoslovakia	LV	Latvia	TJ	Tajikistan
CZ	Czech Republic	MC	Monaco	TT	Trinidad and Tobago
DE	Germany	MD	Republic of Moldova	UA	Ukraine
DK	Denmark	MG	Madagascar	US	United States of America
ES	Spain	MG ML	Mali	UZ	Uzbekistan
FI	Finland			VN	Viet Nam
FR	France	MN	Mongolia		
GA	Gabon				

10

20

25

30

A METHOD OF DEPOSITING TUNGSTEN NITRIDE USING A SOURCE GAS COMPRISING SILICON

The invention relates to processes for fabricating dynamic random access memories, and more particularly to the deposition of tungsten nitride. 15

Tungsten nitride has been shown to be an extremely promising material for planar capacitor and gate electrode applications. Tungsten nitride is stable at high temperatures and prevents dielectric degradation in capacitor applications and acts as a barrier between polycrystalline silicon and tungsten when used as a low resistivity strapping layer in a gate electrode. In one fabrication method Alex Lahav, Karen A. Grim, and Ilan A. Blech, as described in their article, "Measurement of Thermal Expansion Coefficients of W, WSi, WN, and WSiN Thin Film Metallizations," Journal of Applied Physics 67(2), January 15, 1990, page 734, prepare tungsten nitride using reactive sputtering and obtain good film properties.

Although sputtering can provide high quality films, surface step coverage is inadequate for many applications. It would be preferred to have an improved step coverage process such as chemical vapor deposition (CVD).

Nakajima et al. in an article entitled "Preparation of Tungsten Nitride Film by CVD Method Using WF6" appearing in the December 1987 edition of the Journal of Electrochemical Society: SOLID-STATE SCIENCE AND

TECHNOLOGY, has demonstrated chemical vapor deposition of tungsten nitride from NH₃ and WF₆ source gases in a conventional hot wall CVD system. Although hot wall CVD systems offer an advantage with respect to wafer throughput, process control and cleanliness are typically not adequate for state-of-the-art applications. Rather, single wafer cold wall deposition systems are preferred.

For a CVD process WF₆ and NH₃ offer the advantages of being readily available and providing high deposition rates. However, WF₆, NH₃ form an adduct at low temperatures (<50°C), and even with a cold wall system there is a minimum acceptable wall temperature to prevent adduct formation. Furthermore, byproducts of the deposition reactions can cause encroachment into silicon or polycrystalline silicon substrates and therefore the process must be modified to reduce encroachment without compromising adhesion or resistivity.

15

5

10

Thus, there exists a need for a CVD tungsten nitride process having good adhesion and high deposition rates while providing conformal, low resistivity films with minimal silicon encroachment.

20

25

The invention is a method for depositing tungsten nitride using chemical vapor deposition. The method uses a source gas mixture having a silicon based gas for depositing the tungsten nitride to overlie a deposition substrate.

The method is useful in the fabrication of a capacitor electrode, a contact plug, and a gate electrode due to the good adhesion, minimal silicon encroachment and low resistivity of the tungsten nitride deposited according to the method of the invention.

The invention is a non-planar storage capacitor having a tungsten nitride capacitor electrode.

Figures 1-3 are cross sectional views of a semiconductor during various fabrication steps.

Figure 1 is a cross-sectional view of a portion of a semiconductor substrate having various structures fabricated thereon and having a first capacitor electrode.

Figure 2 is the cross-sectional view of figure 1 following the creation of a dielectric layer.

Figure 3 is the cross-sectional view of Figure 2 following the creation of a tungsten nitride electrode.

Figure 4A is a cross-sectional view of a via formed in a substrate and filled with a layer of tungsten nitride.

Figure 4B is the cross-sectional view of Figure 4A following a chemical mechanical planarization of the tungsten nitride layer of Figure 4A.

Figure 5 is a cross-sectional view of a gate electrode having a tungsten nitride barrier layer.

The invention is a tungsten nitride layer formed by a process of the invention in which the tungsten nitride is chemically vapor deposited from a source gas comprising a silicon based gas, such as silane. In one embodiment the invention is a semiconductor non-planar storage capacitor having a tungsten nitride capacitor electrode and is the method for forming the non-planar capacitor. Although the invention is applicable to any number of non-planar capacitors, including trench capacitors and a variety of stacked capacitors, Figures 1-3 depict the process steps for fabricating a stacked capacitor of the invention.

25

10

15

20

25

30

Figure 1 is a cross-sectional view of a partially processed semiconductor device 1 having a buried bit line 5, a wordline 10 overlying a field oxide layer 15, and field effect transistors 20. A thin oxide layer 25 has been removed from a contact area 30 of the substrate 35 and a polycrystalline silicon (herein after also "polysilicon" or "poly") layer 40 has been deposited to overly the substrate 35 and contact the contact area 30 of the substrate 35. The poly layer 40 has been doped and patterned with a photo mask (not shown) to create a storage node plate or first electrode of the capacitor of the invention.

In Figure 2 a dielectric layer 45, preferably tantalum oxide, is deposited to overly the polycrystalline silicon layer 40.

In Figure 3 a tungsten nitride layer 50 is conformally deposited by chemical vapor deposition in a deposition chamber to overlie the dielectric layer 45 thereby forming a second electrode of the storage capacitor. During the chemical vapor deposition a source gas having at least a tungsten source such as tungsten hexaflouride combined with ammonia is combined with carrier gases which may include argon, hydrogen, nitrogen, or other gases. Alternate tungsten sources such as tungsten carbonyl may also be used. In a preferred embodiment the source gas also comprises a silicon based gas such as silane, organic silane, or a compound which is a multiple order of silane, such as di-silane and tri-silane. The source gas is maintained at a pressure conducive to chemical vapor deposition, typically within the range of pressures between 0.1 and 100Torr including the end points. The temperature of the deposition substrate is maintained at 300°C, although other temperatures may be used. The temperature of the deposition chamber walls are held at a temperature which minimizes adduct formation, in this embodiment the walls are held at a temperature greater then 25°C although other temperatures lower than the temperature of the deposition substrate will minimize adduct formation. In one embodiment the source gas comprises tungsten hexaflouride, ammonia, argon, and hydrogen. In this case during deposition of the tungsten nitride layer 20 the tungsten hexaflouride,

ammonia, argon, and hydrogen have flow rates of 50sccm, 150sccm, 80sccm and 80sccm respectively. When silane is added to the source gas mixture the flow rate of the silane is equal to 4sccm which is 1.098% of the total flow rate of the source gas mixture with the added silane.

5

10

In the capacitor of the invention and in other applications the addition of silane to the source gas reduces encroachment into any silicon based materials exposed to the tungsten nitride, improves adhesion of the tungsten nitride to its underlying layer, and reduces the bulk resistivity of the tungsten nitride. For most applications the flow rate of the silane or other silicon based gases should fall within the range of 0.5% to 5% of the total flow rate of the source gas comprising the silicon based gas, although flow rates from .1% to 25% of the total flow rate may be used.

15

It is possible to form the first electrode of the capacitor of the invention using the tungsten nitride when deposited according to the method described above. It is also conceivable that only the first electrode is tungsten nitride. In this case the second electrode overlying the dielectric may be some other material such as polysilicon.

20

In one embodiment the chemical vapor deposition of tungsten nitride using a source gas comprising silane is used to fill a via with tungsten nitride 100, see Figure 4A. Figure 4B shows the tungsten nitride contact plug 105 after chemical mechanical polishing of the tungsten nitride layer 100 shown in Figure 4A. The contact plug 105 contacts the conductive layer 106.

25

30

Alternately the tungsten nitride may be deposited using a source gas comprising silane wherein the deposited tungsten nitride does not fill the via but rather lines the via forming a barrier material. In this case tungsten is deposited to fill the portions of the via not filled by the tungsten nitride.

10

In a further embodiment shown in Figure 5 the chemical vapor deposition of tungsten nitride from a deposition gas comprising silane is used in field effect transistor applications to create a tungsten nitride barrier layer 130 interposed between a tungsten layer 135 and polycrystalline silicon layer 140. In this case exposed portions of the tungsten nitride 130, the tungsten layer 135 and the polycrystalline silicon layer 140 are removed in unpatterned areas to form a gate electrode 45 overlying substrate 150 and gate oxide 160 from masked portions of the tungsten nitride 130, the tungsten layer 135, and the polycrystalline silicon layer 140. In an alternate embodiment no polycrystalline silicon layer 140 is formed and the gate electrode comprises the tungsten nitride 130 and the tungsten layer 135.

Although specific embodiments have been described the invention should be read as limited only by the claims.

CLAIMS:

1. A method for depositing tungsten nitride, comprising the following steps:

providing a source gas mixture comprising silicon said source gas mixture capable of depositing the tungsten nitride;

applying a temperature to a deposition substrate; and

applying a pressure to the source gas mixture to deposit the tungsten nitride from the source gas mixture on said deposition substrate.

- The method as specified in Claim 1, further comprising the step of
 maintaining a temperature of interior walls of a deposition chamber containing said
 source gas mixture at a temperature greater than 25 degrees Celsius.
- 3. The method as specified in Claim 1, further comprising the step of maintaining a temperature of interior walls of a deposition chamber containing said source gas mixture at a temperature which minimizes adduct formation during said step of depositing.
- 25 4. The method as specified in Claim 1, further comprising the step of filling a via during said step of depositing to form an electrical contact in the via.
 - 5. The method as specified in Claim 1, further comprising the following steps:

lining sides of a via during said step of depositing to form a barrier a) layer of tungsten nitride; and

-8-

- filling remaining portions of the via with tungsten, the tungsten b) nitride and the tungsten forming an electrical contact. 5
 - The method as specified in Claim 1, further comprising the following steps: 6.
- creating a first capacitor electrode; a) 10
 - creating a dielectric layer overlying said first capacitor electrode; b) and
- forming a second capacitor electrode during said step of depositing c) 15 the tungsten nitride such that said tungsten nitride overlies the dielectric layer thereby forming the second capacitor electrode.
- The method as specified in Claim 1, further comprising the following steps: 7. 20
 - creating a first capacitor electrode; a)
- creating a dielectric layer of tantalum oxide overlying said first 25 b) capacitor electrode; and
- forming a second capacitor electrode during said step of depositing c) the tungsten nitride such that said tungsten nitride overlies the layer of tantalum oxide thereby forming the second capacitor electrode. 30

10

15

20

- 8. The method as specified in Claim 1, further comprising the following steps:
 - a) forming a first capacitor electrode during said step of depositing the tungsten nitride;
 - b) creating a dielectric layer of tantalum oxide overlying said first capacitor electrode; and
 - c) creating a second capacitor electrode overlying said dielectric layer.
- 9. The method as specified in Claim 1, wherein said step of providing comprises the step of combining at least tungsten hexaflouride, ammonia, argon, and hydrogen to form the source gas mixture.
- 10. The method as specified in Claim 1, further comprising the step of interposing the tungsten nitride between a polysilicon layer and a tungsten layer, said polysilicon layer, said tungsten nitride, and said tungsten layer forming a gate electrode.
- 11. The method as specified in Claim 1, further comprising adjusting a flow rate of the silicon containing gas to be within the range of .1% to 25 % of a total flow rate of the source gas mixture comprising the silicon containing gas.
 - 12. A method for depositing tungsten nitride, comprising the following steps:
- a) providing a first source gas mixture capable of depositing tungsten nitride;

b)	combining silane with the source gas mixture to form a second
	source gas mixture;

c) applying a temperature to a deposition substrate;

- d) applying a pressure to the second source gas mixture comprising the silane; and
- e) depositing the tungsten nitride from the second source gas mixture comprising the silane onto said deposition substrate.
- 13. The method as specified in Claim 12, further comprising the step of adjusting a flow rate of the silane to be within the range of .1 to 25 % of a total flow rate of the source gas mixture.
- 14. The method as specified in Claim 12, further comprising the step of selecting the silane from a group consisting of organic silane and a silane which is
 20 a multiple order of silane.
 - 15. A semiconductor non-planar storage capacitor, comprising:
- a) a non-planar first capacitor electrode;
 - b) a dielectric layer overlying said first capacitor electrode; and
- a tungsten nitride layer overlying said dielectric layer, said tungsten nitride layer forming a second capacitor electrode of the non-planar storage capacitor.

10

15

	16. The non-planar storage capacitor as specified in Claim 15, wherein said dielectric layer is tantalum oxide.
5	17. The non-planar storage capacitor as specified in Claim 15, wherein said tungsten nitride layer comprises silicon.
0	18. The non-planar storage capacitor as specified in Claim 15, wherein said first capacitor electrode is tungsten nitride.
	19. A semiconductor non-planar storage capacitor, comprising:
15	a) a non-planar first capacitor electrode of tungsten nitride;
	b) a dielectric layer overlying said first capacitor electrode; and
20	c) a second capacitor electrode overlying said dielectric layer.
	20. A method for forming a semiconductor non-planar storage capacitor, comprising the following steps:
25	 a) creating a non-planar first capacitor electrode overlying a deposition substrate;
	b) creating a dielectric layer overlying said first capacitor electrode;

creating a source gas mixture for depositing tungsten nitride; and

30

c)

d) depositing the tungsten nitride from the source gas mixture to form a second capacitor electrode of tungsten nitride overlying said dielectric layer.

5

- 21. The method as specified in Claim 20, wherein said step of creating said dielectric layer comprises depositing a layer of tantalum oxide.
- 10 22. The method as specified in Claim 20, wherein said step of creating the source gas mixture comprises combining at least tungsten hexaflouride, ammonia, argon, and hydrogen to form the source gas mixture.
- 15 23. The method as specified in Claim 20, wherein said step of creating the source gas mixture comprises combining at least tungsten hexaflouride, ammonia, argon, hydrogen, and a silicon containing gas to form the source gas mixture.
- 24. The method as specified in Claim 23, further comprising adjusting a flow rate of the silicon containing gas to be within the range of .1% to 25 % of a total flow rate of the source gas mixture.
 - 25. The method as specified in Claim 20, wherein said step of creating the source gas mixture comprises combining at least tungsten hexaflouride, ammonia, argon, hydrogen, and a silane to form the source gas mixture.
 - 26. The method as specified in Claim 25, further comprising adjusting a flow rate of the silane to be within the range of .1% to 25 % of a total flow rate of the source gas mixture.

25

27.	The method as specified in Claim 20, further comprising the follow	/ing
steps:		

a) creating the source gas mixture in a chamber; and

b) adjusting a temperature of interior walls of the chamber to a temperature greater than 25 degrees Celsius.

- 10 28. The method as specified in Claim 20, further comprising the following steps:
 - a) creating the source gas mixture in a chamber; and
- b) adjusting a temperature of interior walls of the chamber to a temperature which minimizes adduct formation during said step of depositing.
- 20 29. A non-planar capacitor fabricated according to a process comprising the following steps:
 - a) creating a non-planar first capacitor electrode overlying a deposition substrate;
 - b) creating a dielectric layer overlying said first capacitor electrode;
 - providing a source gas mixture capable of depositing tungsten nitride;

- d) combining a silicon containing gas with the source gas mixture to form a source gas mixture comprising the silicon containing gas;
- e) applying a temperature to the deposition substrate;

- f) applying a pressure to the source gas mixture comprising the silicon containing gas; and
- g) depositing the tungsten nitride from the source gas mixture

 comprising the silicon containing gas to form a second capacitor electrode of tungsten nitride overlying the dielectric layer.
- 30. The non-planar capacitor as specified in Claim 29, wherein said dielectric layer is tantalum oxide.
 - 31. The non-planar capacitor as specified in Claim 29, wherein said silicon containing gas is silane.

20

32. The non-planar capacitor as specified in Claim 29, wherein said tungsten nitride comprises silicon.

25

33. The non-planar capacitor as specified in Claim 29, further comprising adjusting a flow rate of the silicon containing gas to be within the range of .1 % to 25 % of a total flow rate of the source gas mixture comprising the silicon containing gas.

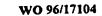
	34.	A capa	acitor electrode made by the process comprising the following steps:
		a)	providing a source gas mixture capable of depositing tungsten nitride;
5		b)	combining a silicon containing gas with the source gas mixture to form a source gas mixture comprising the silicon containing gas;
		c)	applying a temperature to a deposition substrate;
10		d)	applying a pressure to the source gas mixture comprising the silicon containing gas; and
15		e)	depositing tungsten nitride from the source gas mixture comprising the silicon containing gas to form the capacitor electrode overlying the deposition substrate.
	35.	Αg	ate electrode made by the process comprising the following steps:
20		a)	providing a source gas mixture capable of depositing tungsten nitride;
25		b)	combining a silicon containing gas with the source gas mixture to form a source gas mixture comprising the silicon containing gas;
		c)	applying a temperature to a deposition substrate;
30		d)	applying a pressure to the source gas mixture comprising the silicon containing gas;

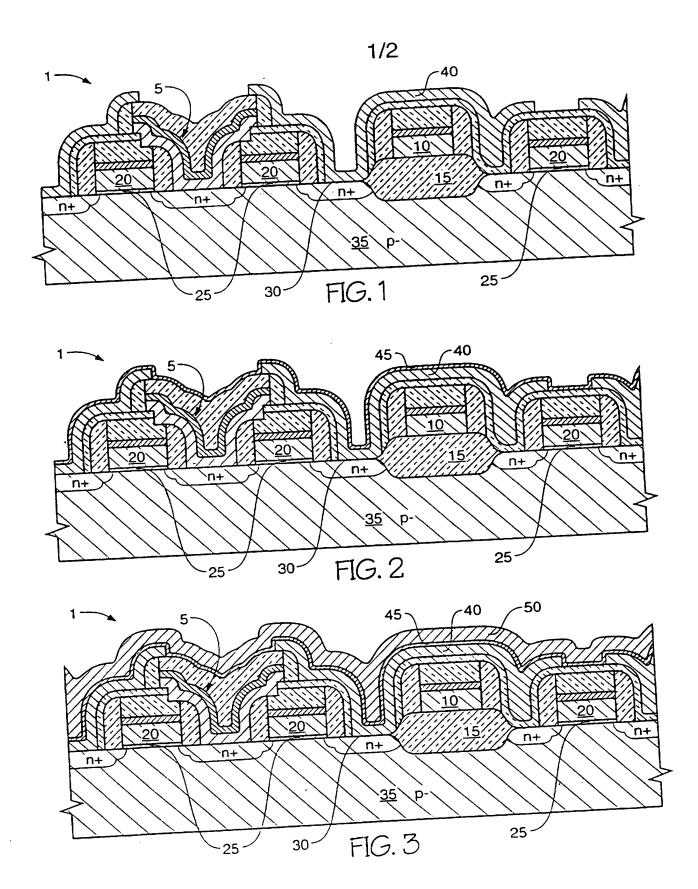
		e)	depositing the tungsten nitride from the source gas mixture comprising the silicon containing gas to form a tungsten nitride layer overlying the deposition substrate;
5		f)	creating a tungsten layer overlying the tungsten nitride layer;
		g)	patterning the tungsten nitride layer and the tungsten layer to define the gate electrode; and
10		h)	removing unmasked portions of the tungsten nitride layer and the tungsten layer, portions of the tungsten nitride layer and the tungsten layer remaining after the step of removing forming the gate electrode.
15	36.	A gat	e electrode made by the process comprising the following steps:
		a)	creating a polycrystalline silicon layer overlying a deposition substrate;
20		b)	providing a source gas mixture capable of depositing a tungsten nitride;
25		c)	combining a silicon containing gas with the source gas mixture to form a source gas mixture comprising the silicon containing gas;
		d)	applying a temperature to the deposition substrate;
30		e)	applying a pressure to the source gas mixture comprising the silicon containing gas;

	f)	depositing the tungsten nitride from the source gas mixture comprising the silicon containing gas to form a tungsten nitride layer overlying the polycrystalline silicon layer;
5	g)	creating a tungsten layer overlying the tungsten nitride layer;
	h)	patterning the polycrystalline silicon layer, the tungsten nitride layer, and the tungsten layer to define the gate electrode; and
10	i)	removing unmasked portions of the polycrystalline silicon layer, the tungsten nitride layer and the tungsten layer, portions of the polycrystalline silicon layer, the tungsten nitride layer, and the tungsten layer remaining after the step of removing forming the gate electrode.
15		
3	37. A de	eposition in a via made by the process comprising the following steps:
20	a)	providing a source gas mixture capable of depositing tungsten nitride;
	b)	combining a silicon containing gas with the source gas mixture to form a source gas mixture comprising the silicon containing gas;
25	c)	applying a temperature to a deposition substrate;
	d)	applying a pressure to the source gas mixture comprising the silicon containing gas; and

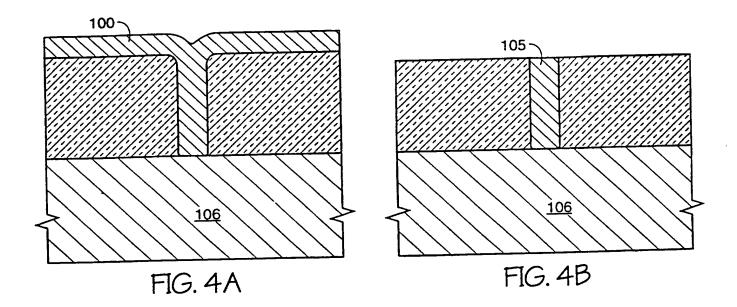
e) depositing the tungsten nitride from the source gas mixture comprising the silicon containing gas to form the deposition in the via.

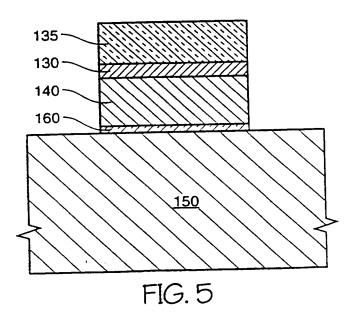
PCT/US95/15559





2/2





INTERITIONAL SEARCH REPORT

			03 307
A. CLASSIFI	CATION OF SUBJECT MATTER C23C16/34 H01L21/285 H01L21/28 H H01L29/47	01L21/3205	H01L21/768
		IPC	·
According to	international Patent Classification (IPC) or to both national classification and		
B. FIELDS S	EARCHED Symbol	s)	
I I PC 6	EARCHED DIMENTATION SEARCHED (Classification system followed by classification symbol C23C H01L		
	that such docum	nents are included in	the fields searched
Documentation	on searched other than minimum documentation to the extent that such documentation the extent that such documentation the extent that the ex		1
1			
	ita base consulted during the international search (name of data base and, wh	ere practical, search	terms used)
Electronic da	ta base consulted during the international		
C. DOCUM	IENTS CONSIDERED TO BE RELEVANT	rerages	Relevant to claim No.
Category *	Citation of document, with indication, where appropriate, of the relevant pa		
X	PATENT ABSTRACTS OF JAPAN	r	15,16, 19-21
^	vol. 018 no. 684 (E-1656) ,22 become	•	
ļ	1994 & JP,A,06 275776 (OKI ELECTRIC IND C	0	
	LTD) 30 September 1994,		
	see abstract		
· I			.
ł			
1			
1			
	Further documents are listed in the continuation of box C.	Patent family me	mbers are listed in annex.
لساا		ater document publi	shed after the international filing date not in conflict with the application but
. Sbear	Carefories of the	or priority date and	shed after the international state of the conflict with the application but the principle or theory underlying the
.V. qo	cument defining the general state of the art which is not madered to be of particular relevance	ru Acuaiou	the desired invention
E, ca	dier document but published on a	Cannot be considered	ten when the document is taken more
fi	ing date	document of particu	llar relevance, are demonster when the
w	tuch is cited to exaction the publication	CARROL OF COMMUNICA	ed to involve an inventive step ned with one or more other such docu- nation being obvious to a person skilled
.0. 9	ocument referring to an oral disciouse, use,	ments, such contra	2501. 0000
	ther means ocument published prior to the international filing date but ater than the priority date claimed	document member	of the same patent family
l t	of the actual completion of the international search	Date of mailing of	the international search report
Date	M file strings continues	1 0. 04. 99	Ĝ
]	25 March 1996		
	the ISA	Authorized officer	
Name	European Patent Ullice, P.B. 3010	es :	F
	NL - 2280 HV KIRWIE Tel (+ 31-70) 340-2040, Tx. 31 651 epo nl.	Flink,	E .
1	Fac (+ 31-70) 340-3016		

Form PCT/ISA/219 (second sheet) (July 1992)